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Initiation Identification in Fused Silica 355-nm Optics

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ABSTRACT

Thermo-mechanical surface damage initiation and growth in fused-silica 3ω (355nm) optics are important performance and cost issues for high-power lasers (fluences of 4-14 J/cm^2) in the few ns pulse length regime. We are working to characterize and identify the extrinsic origins of damage initiation; impurities, particulates, and manufacturing defects. We have performed a materials characterization survey approach using transmission electron microscopy to identify the chemistry and morphology of particles, and structural defects. TEM offers high chemical or elemental specificity and small analytical spot size yielding complementary materials characterization data and powerful *clues* to manufacturing improvements. We will report on our characterization of the near surface of one commercially manufactures fused silica optic, where the results indicate both the efficacy and potential value of this approach.

Keywords: Fused-silica, Transmission electron-microscopy, Cracks, Particles

1. INTRODUCTION

Recently, with the utilization of magneto-rheological-finishing (MRF), there has been important progress in the improvement of the resistance to surface damage of fused-silica optics exposed to high fluence (4-14 J/cm^2) 355nm (pulse length 3ns to 8ns) light [1]. Although progress has been significant, there still remains the uncomfortable *lack-of-knowledge* about what defects were avoided, and more importantly, what defects and manufacturing improvements or approaches to focus on to achieve future improvements. The underlying hypothesis for past and future improvements is an acceptance of the idea that there is not one, but many possible causes of surface initiated damage [2, 3, 4]. It has been noted repeatedly, and most recently [4], that polishing of fused silica is a chemo-mechanical process that results in the formation of a thin redeposit ion or Beilby-layer [5]. The Beilby-layer contains contaminants associated with the polishing process itself, most notably CeO_2 polishing compound that absorbs strongly in the UV, giving rise to the characteristic "gray-haze" damage morphology [4]. This layer may also "mask" other near-surface defects such as cracks and particulate associated with all the manufacturing stages; grinding thru the final polishing. The removal of the Beilby-layer by wet etch has served to reveal that these other sources of damage initiation do exist. For the fluences and pulse lengths mentioned above, it is accepted [3] that either the electric field is enhanced, or that the energy is absorbed at surface and near surface defects or particles, e.g., surface scratches [6], or sub-surface structures, to initiate damage. Characterization of these initiation sites and their control or removal, are important for technological progress in high-fluence fused-silica optics. Recent experiments, which studied the damage characteristics of deterministic defects (gold particles and scratches) [7], when considered with the analytical materials characterization reported here, result in a qualitative understanding of how MRF improves fused silica damage performance and what approach one should take for further improvements.

2. EXPERIMENT

2.1 Fused-silica specimens

Vendor-polished Corning 7980 fused silica was used to manufacture a 45cm-by-45-cm optical flat. The polishing process utilized a CeO_2 final grit and also employed a buffered HF etch in the polishing process with the last etch removing 1.0μm of the final polished material. Specimens used in this work (2.5cm by 2.5cm) were cut from this plate. The optical surfaces were protected during cutting with a lacquer material *Modalac,* which was subsequently removed by organic solvent. The optical surfaces were cleaned using a procedure involving colloidal alumina and a final drag wiping.

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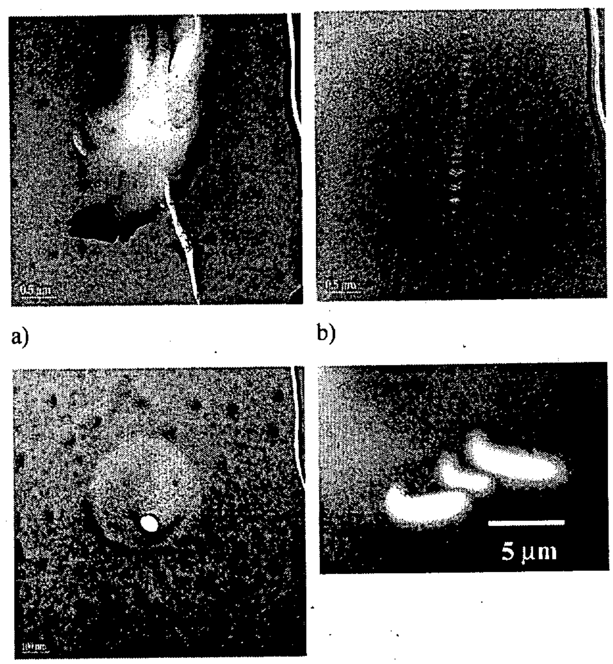
2.2 Preparation of TEM specimens

Random cross-section and planview transmission electron microscopy (TEM) samples were prepared. The cross-section samples showed no distinct microstructural features and this approach was abandoned. In a cross-section specimen the total amount of surface that is viewed in a single specimen is not much more than 1 sq. μm, hence the probability of sectioning through a small microstructural or surface feature is very small. The planview samples (~100nm thick with one surface being the as prepared optical surface) exhibited a variety of microstructural and surface features. The features may be classified into two groups; surface irregularities or mechanical defects (cracks, digs, etc), and particulate structures on the optical surface and buried.

3. MATERIALS CHARACTERIZATION

3.1 Observation and characterization of mechanical defects

The observed near-surface or surface irregularities can be sub-divided into three groups: mechanical indents, pits and smooth surface depressions. Figure 1 illustrates these three types of observed near-surface irregularities seen in planview TEM specimens. In Figure 1a, a mechanical looking divot is shown. The bright regions within the central part of the divot is the shallow portion and the darker annular region is where there is either a thicker brim around the divot protruding up from the polished surface and/or the region is a more dense form of SiO_2. Energy filtered imaging thickness maps of several divots show that they are quite shallow, 10nm to 50nm deep. These divots often ($\approx$ 20%) had cracks (median structures perpendicular to the optical surface) associated with them. All of the cracks seen are very narrow (<50nm) and range in lengths from 10nm to 10μm. The depth measurement of the cracks was sometimes less than the thickness of the sample (i.e. $\approx$ 100nm) and sometimes greater than the thickness of the specimen. Hence, some cracks are truncated by the finite thickness of the specimen. Often the divots have one or more divots near by that are similar in morphology but not as deep. Chemical analyses of these divot regions do not show any specific chemistry associated with them. The cracks all appear to be empty. In Figure 1b a linear row of smaller divots are seen. We call this micro-chatter. Typically these do not have densified or thicker annular regions around any one divot. The chemistry associated with these chatter marks is also not abnormal, and there does not appear to be any cracks associated with these chatter marks. In Figure 3c we observed a pit that goes through the specimen. Stereo analysis confirms this. In Figure 1d we see shallow surface depressions that are very smooth looking, unlike the divots in Figure 3a. There does not appear to be cracks or unusual chemistry associated with these surface depressions. The total number of defects seen by planview TEM in 4 samples was $\approx$ 65. Approximately 75 % of the defects were of the mechanical nature as in figures 1a and 1b, with $\approx$ 20% of these having cracks associated with them. Approximately 15% of the defects were pits as in Figure 1c and the remainder being defects seen in Figure 1d. In all, the total area sampled by planview TEM was $\approx$ 400 μm^2, thus the population of these defects is $\approx 2.5 \times 10^3 / mm^2$.



a) b) c) d)

Figure 1: Mechanical damage observed in polished and acid etched fused silica specimens. a) densified "divot-site" with accompanying median crack; b) an example of what we call micro chatter consisting of a series of "divot-sites" similar to those seen in panel d); c) small isolated divot or "dig" which passes through the 100nm specimen; d) chatter marks without cracks.

3.2 Elemental composition of particles

In all of the planview specimens, there was high density of surface debris. Most of this was probably from the Modalac. Stereo pair analysis confirmed that this debris was on the surface. We also observed a region of microstructure other than amorphous SiO_2 where stereo analysis showed that there was particulate *within* the SiO_2 specimen. Figure 2a is an image of this structure. Energy filtered TEM showed that the amorphous component contained carbon. In addition, energy dispersive spectroscopy (EDS) analysis (shown in Figure 2b) for this area showed that there were other elements present. Additional elements detected included; Cu (as a resolvable 100nm particle with enough Zn present to possibly be brass), Ca, Mg and Al. Electron diffraction showed that there was some crystalline component to this structure but we were not able to index the spots to any particular phase. The *Analytical Phillips 300 KeV FEG* (field emission gun) transmission electron microscope (TEM) is both a powerful near atomic resolution imaging tool, and an analytical instrument capable of providing chemical information with a few nm analytical spot size utilizing energy loss spectroscopy.

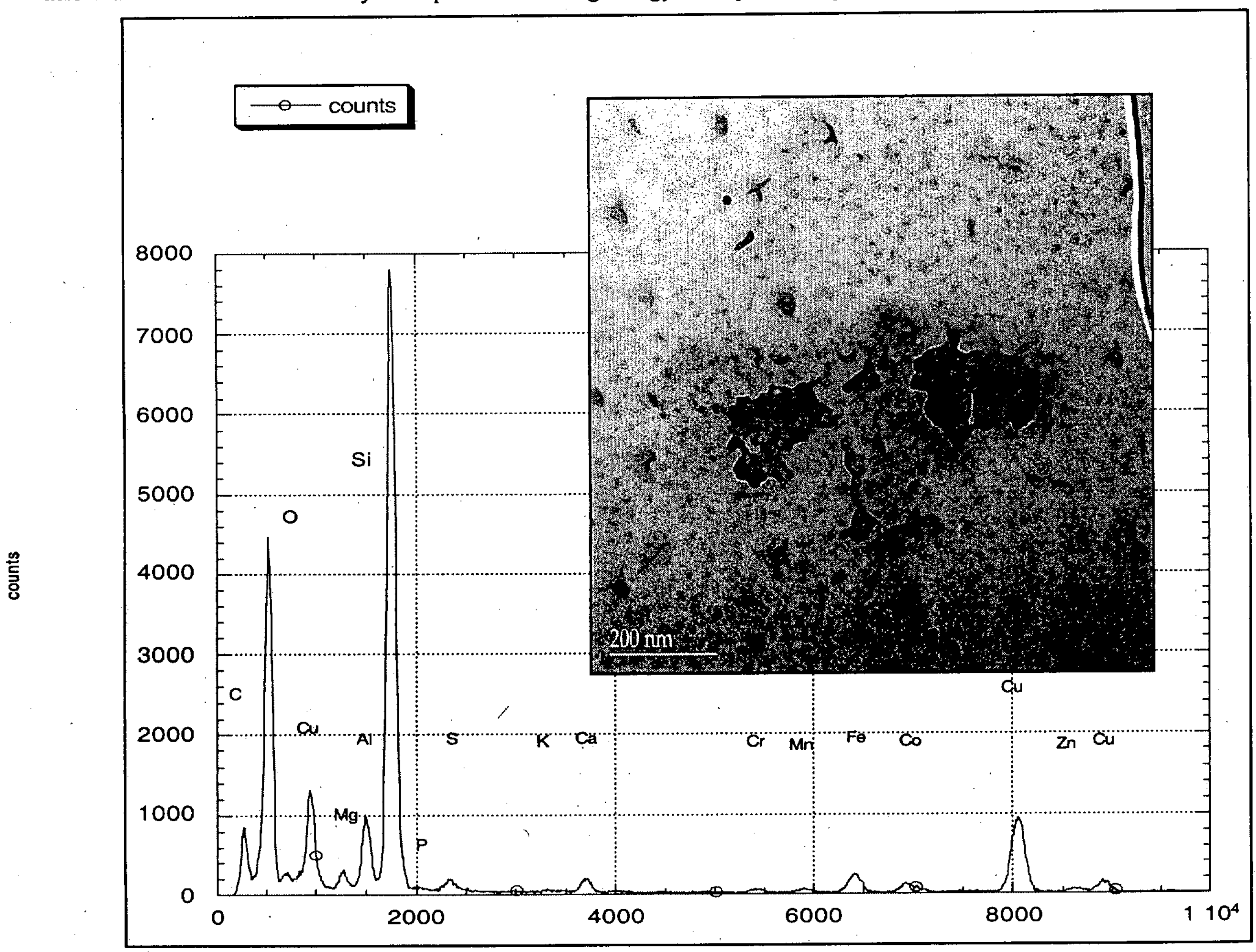
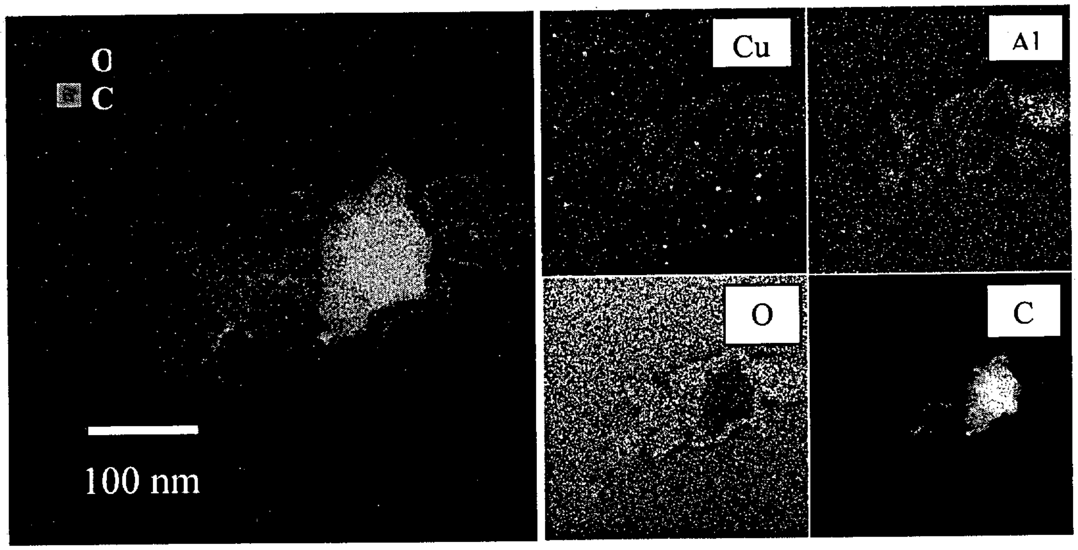


Figure 2: a) (top) TEM micrograph of a near surface included particle. b) (bottom) EDX spectrum (counts vs eV) from the area of the inclusion showing the presence of carbon and copper.

Having observed particulate with EDS and TEM that was imbedded within the near surface of our fused-silica specimens we set out to search more carefully and to characterize in more detail any other particles that we could discover. Figure 3 is typical of what we saw. We observed a quite complex particle made up of several morphologies and several elements. There is a carbon rich region that is depleted in oxygen, which on further analytical analysis suggests that its diamond or diamond-like material. The same particle is also rich, in some areas, with aluminum, but here there is a correlation with oxygen suggesting alumina. Finally, there is clear evidenced for a population of ~5nm diameter particles that are Cu rich. Atomic resolution imaging shows that these particles are indeed crystalline since their atomic columns could be imaged for some fortuitous orientations. The particles observed here were proven, using several TEM analytical techniques including stereomicroscopy and energy loss methods, to be below the surface of the finished optic. It is worth noting that our attempts to observe such particulate (in the bulk-region well below the surface yielded negative results, consistent with the results from cross-sectional specimens studied earlier.



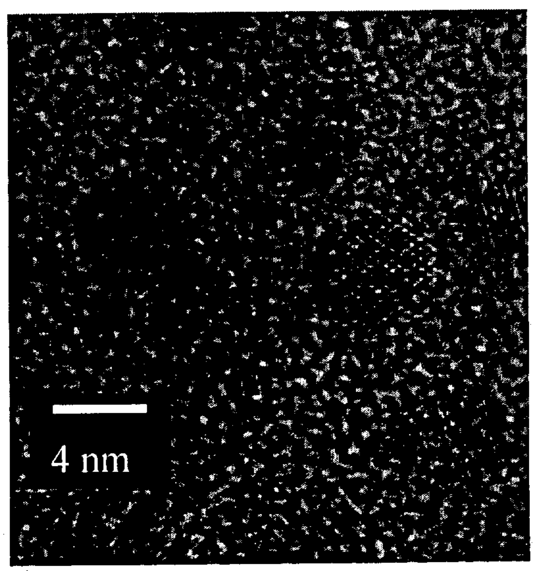


Figure 3: In these micrographs we have visualized a complex particle imbedded in the near surface region of the fused-silica. The Phillips FEG TEM makes available extensive chemical characterization and near atomic resolution. The upper pictures (large and four smaller replicas) illustrates a carbon based particle (~80nm diameter surrounded by an oxygen rich matrix, Additionally, there is evidence for Al (Al_2O_3) and many small copper particles. The lower micrograph shows us that the nm-size copper (possibly copper alloy) particles are indeed crystalline by revealing columns of atoms in those nano-grains oriented appropriately to the electron beam of the TEM.

4. DISCUSSION

4.1 Cracks and mechanical damage

Cracks, particularly median cracks, such as those observed in this work are a consequence of the balance between productivity and perfection in the polishing of fused silica optics. Can such cracks be initiation sites in themselves? As shown in recent results of Genin and co-workers [8] and Hamza and co-workers [7] this is quite possible. Additionally, it is often observed that initiation sites lie along lines or trajectories suggesting a high spatial correlation with some cracks. The open question is, are these mechanical features alone potent initiators or does sufficient energy absorption require impurities as well. Admittedly, the results of [7] are a special case, but it is demonstrated that cracks arising from slow scratches are sufficient alone to act as initiation sites in a range of fluences of technological relevance. The present TEM results strongly suggest that this question deserves further modeling and experimental investigation. As additional empirical evidence for the importance of mechanical defects as a source of potent initiation sites, we site the work reported in these proceedings by Menapace and co-workers (1). The authors compare conventionally polished fused silica and MRF polished using total internal reflection microscopy as a defect visualization tool. It is well known that only a fraction of the defects visualized with TIRM are potent initiation sites but as shown in their work the MRF leads to a dramatic reduction in observable TIRM defects and a corresponding large reduction in damage density at technologically relevant fluences (4-14 J/cm^2). The idea suggested is by reducing the number density of all the defects one also reduces the potent sites as well. This is what makes the TEM studies relevant.

4.2 Particulate as initiators

For the fused silica specimens studied here particulates are a significant feature. Thermo-mechanical calculations show that temperatures high enough to cause damage are only likely if the contaminant was present as particles with diameters of >10nm (4, 9). The sizes of the carbon (likely diamond) and copper alloys (brass) particles are, in some cases, sufficiently large to be potent initiators. Pure diamond would also be expected to be transparent at 355nm. However, industrial diamonds that would have been used in the grinding phase of manufacturing would not be. The origin of the copper is likely from the same grinding process, as most grinding wheels or pads are manufactured with a brass substrate embedded with diamond grit. A possible scenario for the origin of the aluminum may be associated with the extensive use of colloidal alumina. Even here, although alumina should be transparent at 355nm, industrial grade material appears to absorb energy due to chemical impurities common in its production.

5. CONCLUSIONS

The exact way in which these impurities and mechanical defects entered the specimen is, to a large degree, speculation. That they are present, is not. Are they initiators, particularly the median cracks? That question requires further investigation as well. One can not, and should not generalize the results of the materials characterization reported here. We have demonstrated the powerful sensitivity and characterization capabilities of analytical TEM in helping to provide clues and evidence for the origins of damage initiation. If there is one important new piece of knowledge, it is that polishing in the ductile regime, where the possibility for median cracks is virtually eliminated, is not only a good idea as suggested by this work and reference (7), but as evidenced in (1), an idea that works. Hence, the TEM work provides some structure-property evidence for why MRF yields such dramatic improvements in surface damage densities.

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